

LUMINESCENCE SPECTRA OF THE URANYL ION IN TWO GEOMETRICALLY
SIMILAR COORDINATION ENVIRONMENTS: URANYL NITRATE HEXAHYDRATE
AND DI- μ -AQUO-BIS(DIOXODINITRATOURANIUM(VI)) DI-IMIDAZOLE

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Luminescence Spectra of the Uranyl Ion in Two Geometrically
Similar Coordination Environments: Uranyl Nitrate Hexahydrate
and Di- μ -aquo-bis(dioxodinitratouranium(VI)) Di-imidazole.

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ABSTRACT

The luminescence spectra of the uranyl ion have been obtained at room and liquid nitrogen temperatures in the crystal hosts of uranyl nitrate hexahydrate (UNH) and di- μ -aquo-bis(dioxodinitratouranium(VI)) di-imidazole (UNI). In both coordination spheres, the uranyl ion lies at the center of similar, distorted coordination hexagons consisting of two bidentate nitrate groups and two water molecules; the only difference in the coordination geometries is that the water molecules are terminal in the UNH complex and bridging in the UNI complex. The uranium-uranium "bond" distance in the UNI complex is 3.93 Å. At room temperature, the emission spectra of the two compounds are essentially identical, but significant differences appear upon cooling to 77°K. Vibronic structure is observed in the crystal of the UNI complex but not in the crystal of uranyl nitrate hexahydrate; this implies that the geometry of the uranyl ion in the two excited states is somewhat different. An energy level sequence is presented in which the various emission lines arise from a slightly split excited state (splitting approximately 80-85 cm⁻¹) to several vibrational levels of the ground electronic manifold. The energy spacing of the ground vibrational levels (approximately 860 cm⁻¹) was found to vary when changing crystal systems.

INTRODUCTION

The luminescence associated with the uranyl ion has been known for quite a long time, and it has been observed that this emission is sensitive both in lineshape and in wavelength maxima to details of the coordination environment.² The uranyl ion possesses a rich photochemistry, and the luminescence may be quenched by a considerable array of energy acceptors.³ Nevertheless, in spite of the number of studies carried out with this ion, the nature of the emitting state has remained elusive until fairly recently. A detailed analysis of spin-orbit coupling and one-electron energy differences in the 5f shell combined with spectroscopic data enabled Jorgensen and Reisfeld⁴ to conclude that the lowest excited level is of even parity, has no well-defined S and Λ , and has a quantum number of $\Omega = 4$.

Perry and coworkers⁵ have recently reported the synthesis and crystal structure of di- μ -aquo-bis(dioxodinitratouranium(VI)) di-imidazole (UNI), a water-bridged dimer of uranyl nitrate. The central coordination sphere in this dimer consists of two bidentate nitrate groups in addition to the two bridging water molecules that occupy the fifth and sixth equatorial coordination sites of the two uranyl ions. The uranium atoms in the dimer are separated by a distance of 3.93 Å, and each water molecule in turn has one imidazole unit hydrogen bonded to it. The coordination sphere of donor ligands about the uranyl ion in this complex is identical to that present in uranyl nitrate hexahydrate (UNH)⁶ except that the water molecules in the latter complex are terminally bonded. The uranyl ion in both complexes lies at the center of a

distorted hexagon of oxygen donor atoms associated with the nitrate and water groups (see Figures 1 and 2).

In the present work, single crystal luminescence spectra have been obtained for uranyl nitrate hexahydrate and di- μ -aquo-bis(dioxodinitratouranium(VI)) di-imidazole at room and liquid nitrogen temperatures. The low-temperature, high resolution spectra have enabled an experimental mapping of energy levels, and the close correspondence of crystal structures allows certain conclusions to be drawn regarding the influence of both the water and hydrogen bonded imidazole molecules on the energy levels of the uranyl ion in the two complexes.

EXPERIMENTAL

Single crystals of uranyl nitrate hexahydrate (Baker Chemicals) were grown by slow evaporation from an aqueous solution, and the crystals of di- μ -aquo-bis(dioxodinitratouranium(VI)) di-imidazole were the same as those used in the single-crystal x-ray diffraction structural study.⁵

Luminescence spectra were recorded on a high-resolution emission spectrometer constructed in the laboratory of one of the authors (H.G.B.). The 365 nm output of a 200-watt Hg-Xe arc lamp was selected by a combination of a 0.1 m grating monochromator (Model H-10-UV-V, Instrument SA) and UV-transmitting "black glass" filter and then focused onto the sample crystals. For low-temperature work, the crystals were contained in a suprasil quartz tube and immersed in liquid nitrogen. The emission was collected at 90° to the

exciting beam, analyzed by a 0.5 m grating monochromator (Model 1870, Spex Industries), and detected by an EMI 9797B photomultiplier tube (S-20 response). An emission bandpass of 15 Å yielded maximum resolution at room temperature, but at liquid nitrogen temperature, a bandwidth of 5 Å was necessary to achieve optimum resolution. No attempt was made to correct the emission spectra for monochromator or photomultiplier response. Excitation at wavelengths other than 365 nm did not lead to any differences in the luminescence spectra, except for intensity changes that were consistent with variations in the degree to which the excitation energy was absorbed.

RESULTS AND DISCUSSION

At room temperature, the luminescence spectra of UNH and UNI are almost identical, as is shown in Figure 3. The uranyl emission recorded for both systems closely resembles the spectrum obtained for the uranyl ion in water,² which indicates that all emission lines found in the crystal originate from the uranyl ion alone. No luminescence is observed in the UNI crystal spectrum that can be assigned to imidazole. For both crystal systems, a total of four luminescence bands are observed, and the wavelength maxima of these bands correspond closely in the UNI and UNH systems. Three of the bands are located at the same wavelength (510, 533, and 558 nm), while the band at the highest energy is found to exhibit a slight crystal system dependence (488 nm for the UNH complex and 491 nm for the UNI complex).

To clarify these spectral differences further, low-temperature emission studies have been conducted. As would be expected, the emission intensity

increases, and each feature at room temperature splits into at least two components. The wavelength maximum of each band shifts toward higher energy, implying that the room temperature emission consists primarily of transitions containing a considerable vibronic component. At liquid nitrogen temperature, the three bands at highest energy persist, but the last band at 558 nm completely disappears. The emission spectra for the three remaining bands (which are labeled A, B, and C in order of decreasing energy) are shown in Figures 4-6 for both the UNI and UNH crystal systems.

The difference in the environment about the two types of uranyl ions in the UNI and UNH crystals is clearly apparent in the low-temperature spectra. An examination of Figures 1 and 2 reveals the close correspondence between the crystal structures, but the emission spectra reveal slight differences in wavelength maxima, and it would appear that vibronic phonon structure is present in the spectrum of the UNI complex while being absent in the spectrum of the UNH complex. Positions of all emission bands are found in Table I, while wavelength maxima and transition energies for the UNI spectral bands are shown in Table II. A comparison of emission intensities associated with the UNI and UNH complex crystals is difficult due to the problem of attaining similar geometrical arrangements of the crystals, but it would appear that the uranyl emission in the UNI compound is approximately three times as intense as that in UNH.

The detailed nature of the uranyl emission in the UNI crystal permits the assignment of all peaks in the A, B, and C systems. An examination of the

energies of the emission lines leads to the conclusion that two electronic transitions are present in each band system; the remaining peaks are due to coupling of lattice phonons with these electronic transitions. For each band system, two weak origins are noted at highest energy and a series of more intense peaks follows. It is a general feature that the origin at highest energy has vibrational lines occurring every 170 cm^{-1} , while the other origin has vibrational energy spacings of approximately 190 cm^{-1} . These vibrational energy spacings appear to remain relatively constant for corresponding origins in all emission band systems. Assignments of the vibronic structure are given in Table II.

It is highly interesting to note that no vibronic structure is present in the spectrum of the UNH compound. A comparison of the UNI and UNH transition energies would imply that all UNH emission bands actually correspond to $v_{1,2} = 1$ transitions and that these are not very intense origins. Given the close structural similarity of the two uranyl complexes, this conclusion would appear reasonable. A search at high sensitivity for the electronic origins corresponding to the $v = 0$ emission reveals nothing at 77°K . It is generally accepted that the absence of vibronic structure in solid state luminescence spectroscopy indicates that the geometry (i.e., bond lengths and angles) of the excited state is essentially the same as that of the ground state. Conversely, a long progression indicates a large difference in the geometries. The absence of any vibronic structure for UNH implies that no geometry changes take place upon excitation, but the medium progression seen for UNI appears to

indicate that the geometry of the excited uranyl ion in this crystal system changes upon excitation.

Two other trends may be outlined from a consideration of the data in Tables I and II. The energy separation between corresponding $\nu_{1,2}$ lines in both the UNI and UNH emissions for the A, B, and C band systems is very nearly constant for each type of crystal. In the case of the UNH compound, this energy separation is found to average 866 cm^{-1} , while the separation is 853 cm^{-1} for the UNI complex. It is well known that the totally symmetric vibration of the uranyl ion has an energy of 856 cm^{-1} ,⁷ so that it would appear that the A, B, and C emission systems correspond to emission from the excited state to several vibrational states of the ground state manifold. The observation that the energy of this totally symmetric vibration is different in the UNH and UNI complex crystals is another indication of some difference in the uranyl environments in the two systems.

Another interesting feature observed is that two electronic transitions are found in each band. For both the UNI and UNH crystal systems, the energy separation between the components having the same value of ν within each band system is essentially the same. For the UNH compound, this separation is 82 cm^{-1} , while the separation in the UNI complex is 85 cm^{-1} . This difference between the UNI and UNH is probably not significant, and the authors believe that the same mechanism operates in both crystal systems.

All of these conclusions enable the determination of an empirical energy level diagram relating the uranyl ion luminescence in both crystal systems,

and this diagram is shown in Figure 7. The A, B, and C emission bands are observed to arise from emission of a pair of almost-degenerate excited states to the vibrational levels within the ground state. The lattice vibrations couple with each of the six transitions shown, and the observation that the phonon energy is the same for each transition band indicates that the excited state is split by the 80 cm^{-1} value (another possibility that might be considered is that each ground vibrational level is split by 80 cm^{-1} but has been rejected due to the phonon energy being so constant).

The small differences that are detected in the energy levels of the uranyl ion when it is placed in the UNH and UNI compounds demonstrate the sensitivity of these levels to the coordination environment. The emitting state is almost certainly of f-orbital in origin,⁴ and the influence on these orbitals by chemical bonding is evident. Given the identical coordination donor set of ligands about the uranyl ion in both cases, the difference in the electronic properties of the uranyl species in the two crystal systems is most likely due to some long-range effect. In the UNI complex, two uranyl ions are bridged by water ligands with imidazole molecules hydrogen-bonded to them, and it is possible that the observed effects are due to weak coupling between the two uranium(VI) metal centers. It is equally possible that there exists a long-range effect of the hydrogen-bonded imidazole molecules on the uranyl ion in the UNI crystal, and a similar effect of the noncoordinated lattice water molecules in the UNH complex may also be postulated. The inherently greater luminescence associated with the UNI system relative to that of UNH does suggest that some amount of energy transfer may be occurring. At the present

time, it is not possible to partition the amounts of the contributions from these several potential effects.

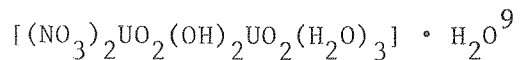
ACKNOWLEDGMENTS

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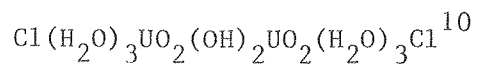
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8. The uranium-uranium bond distance of 3.927 Å in di-μ-aquo-bis(dioxo-bis(nitrato)uranium(VI)) di-imidazole is the shortest reported length

between two uranyl ion centers, and it thus affords the best opportunity to date for detecting metal-metal coupling in the UO_2^{+2} system. Two other bridging uranyl dimers (which possess bridging hydroxy groups instead of water) that have quite similar bonding are the



and



complexes which have uranium-uranium distances of 3.939 Å and 3.944 Å, respectively.

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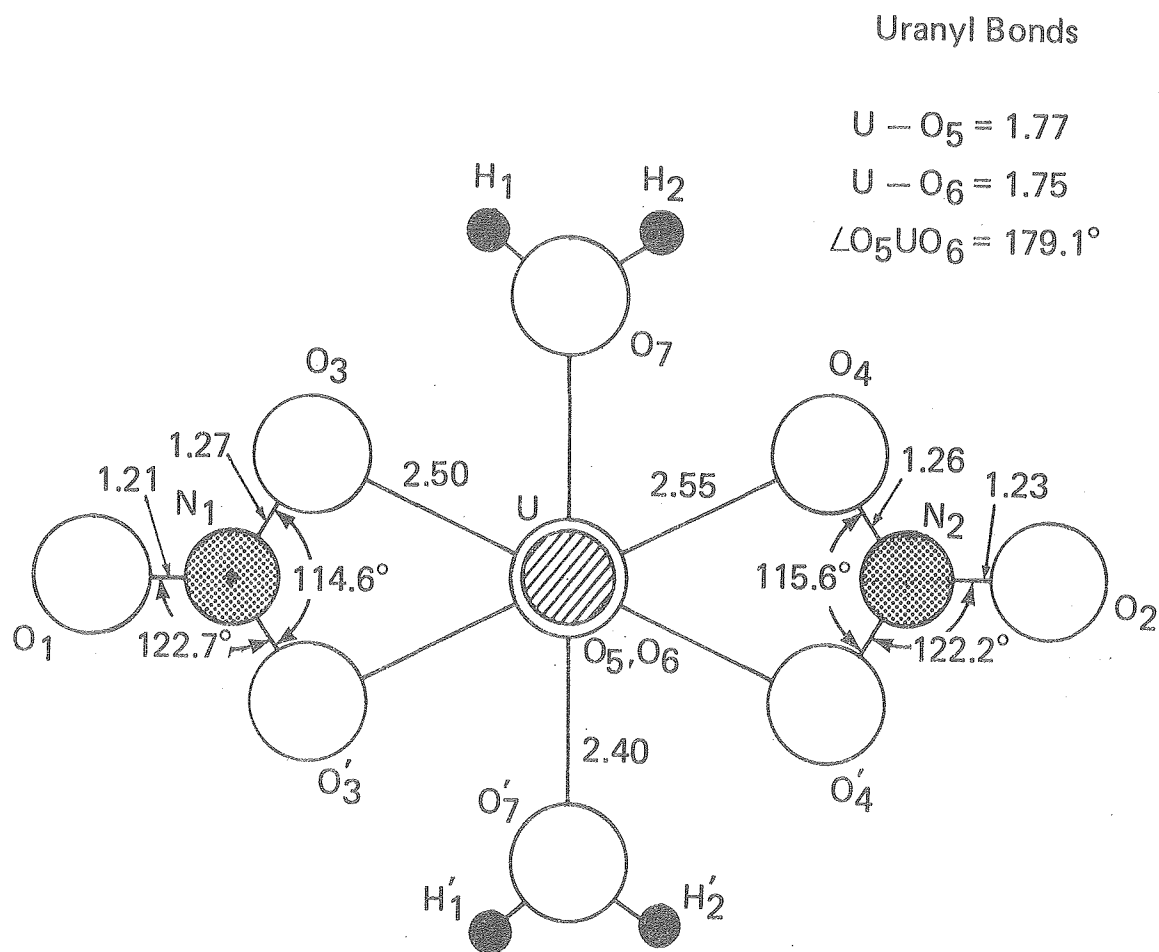
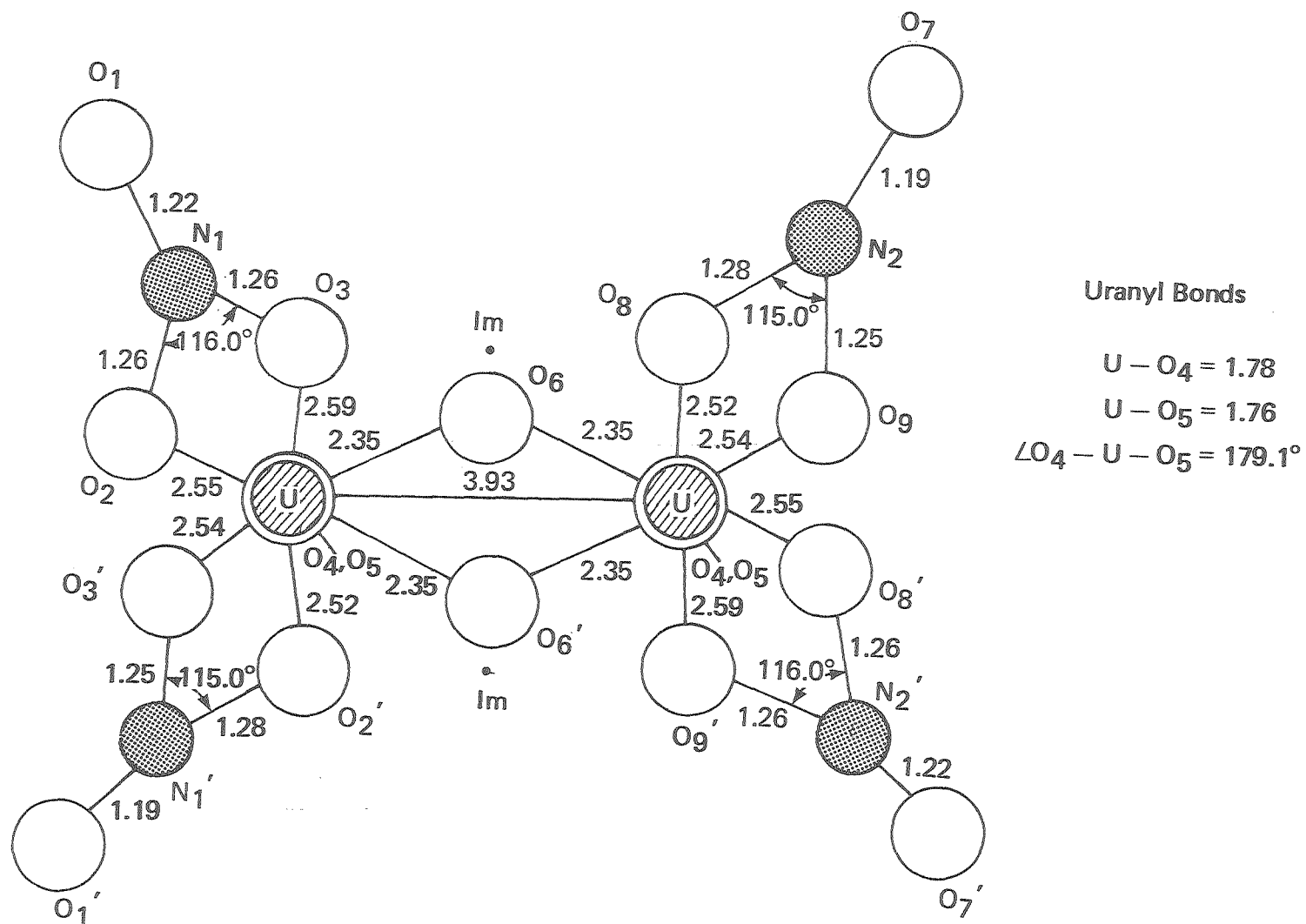


Figure 1. The coordination sphere of uranyl nitrate hexahydrate (UNH).



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Figure 2. The coordination sphere of di- μ -aquo-bis(dioxodinitratouranium(VI)) di-imidazole. For the sake of clarity, the structural details of the imidazole (Im) molecules hydrogen bonded to the bridging water ligands have been omitted.

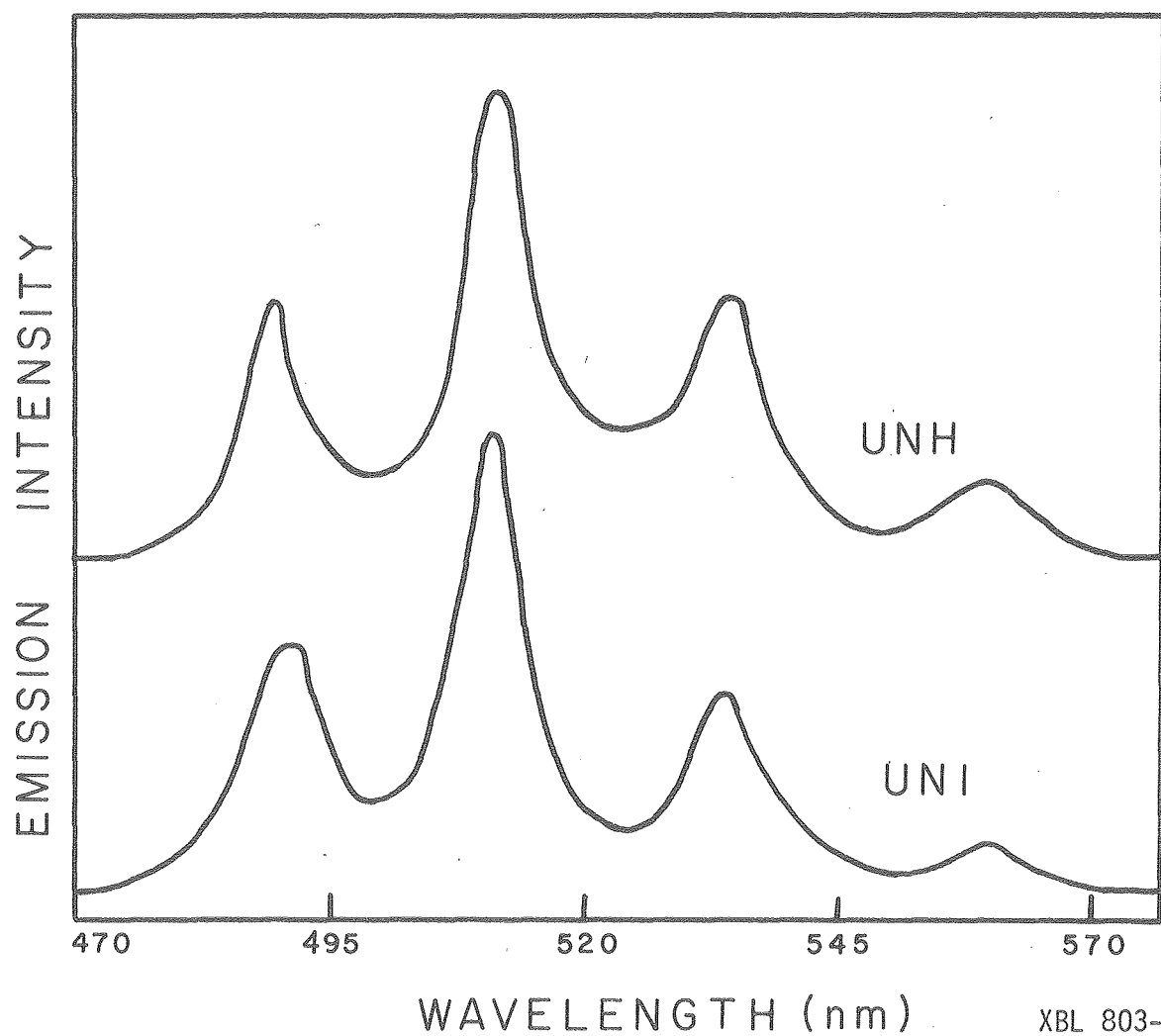
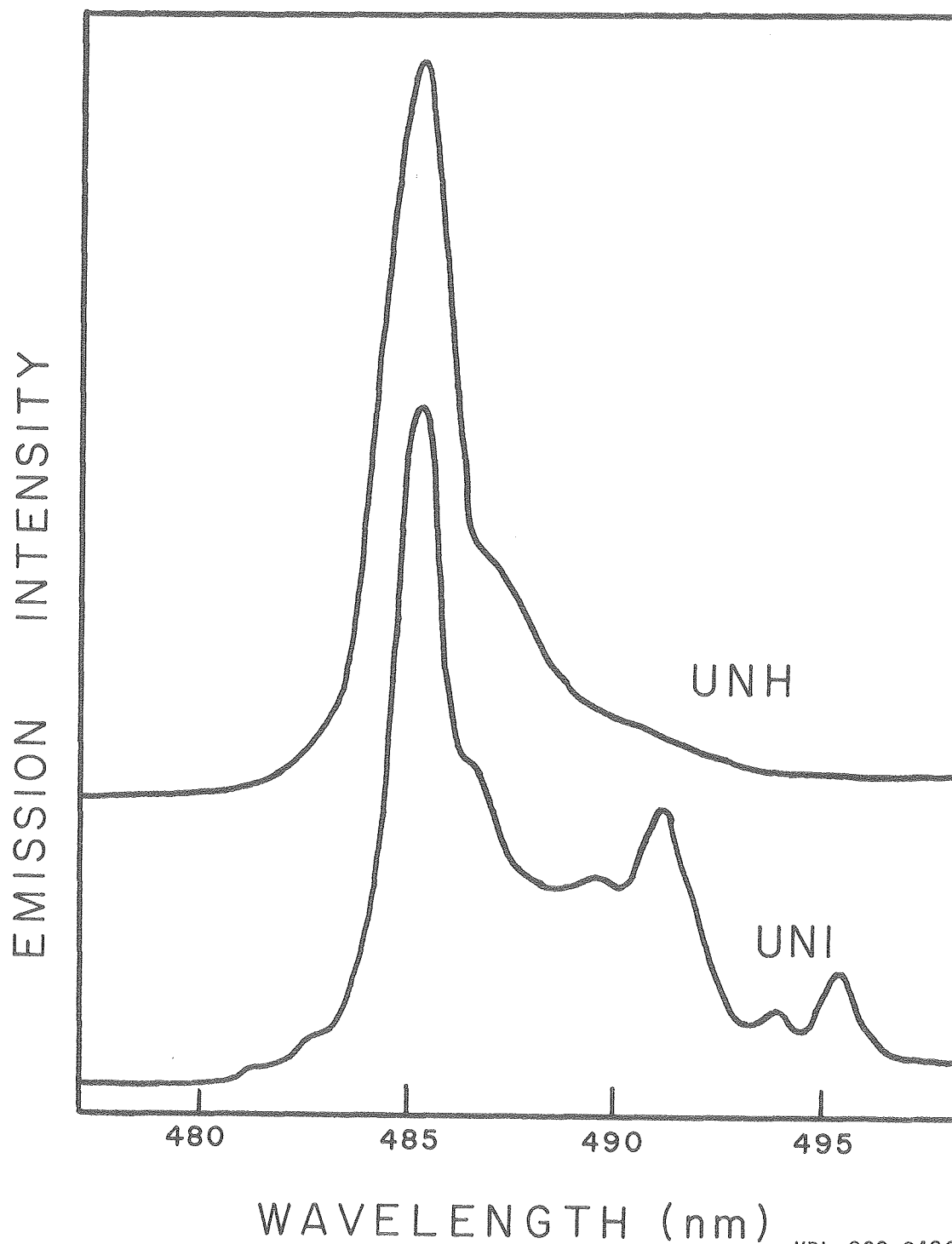


Figure 3. Room temperature luminescence spectra of the uranyl ion in the UNH (upper) and UNI (lower) complexes. The intensity scales are completely arbitrary and are not comparable.



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Figure 4. Luminescence at 77°K for the UNI (lower) and UNH (upper) complexes; this emission is from band system A. The intensity scales are arbitrary.

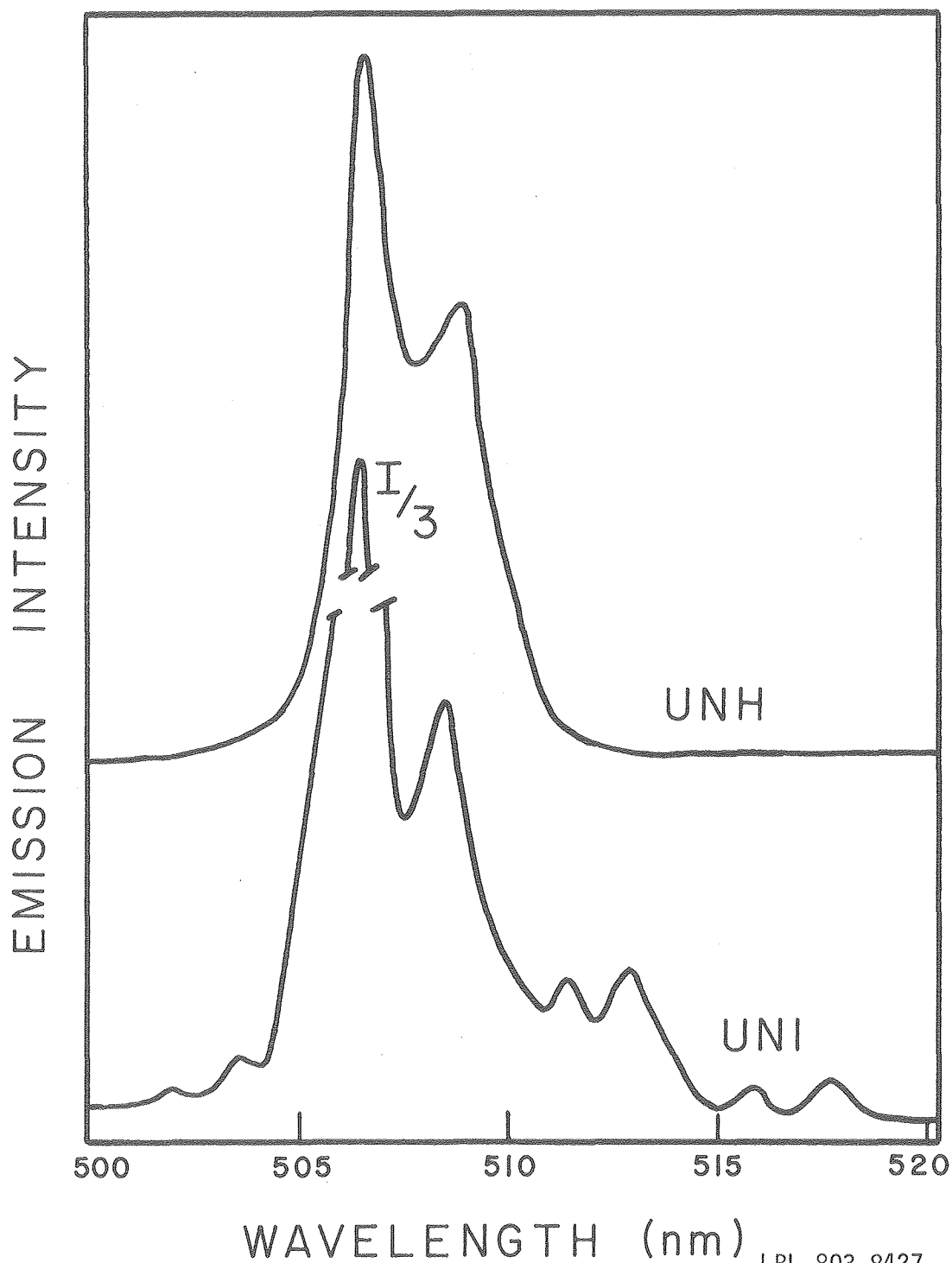
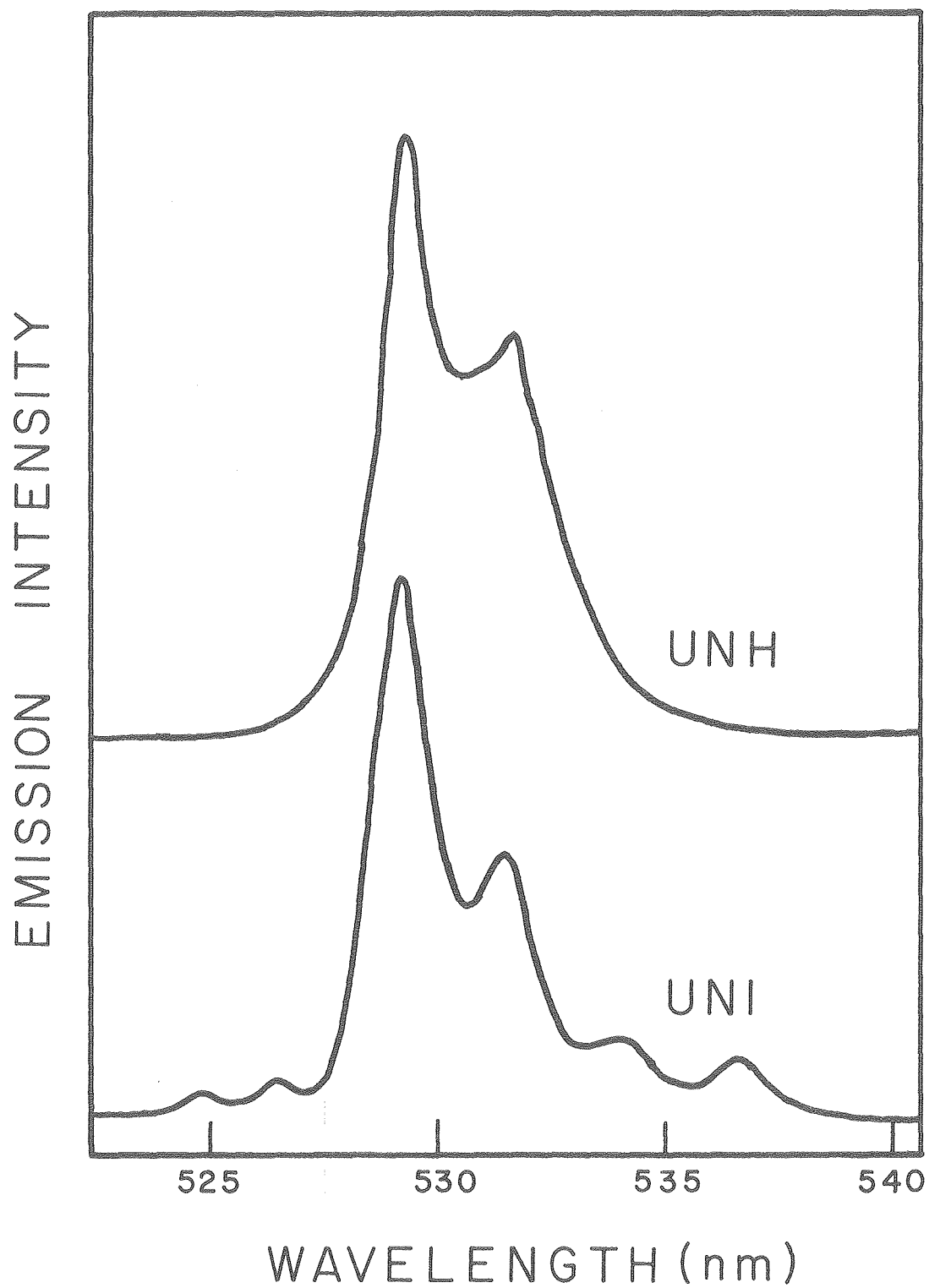
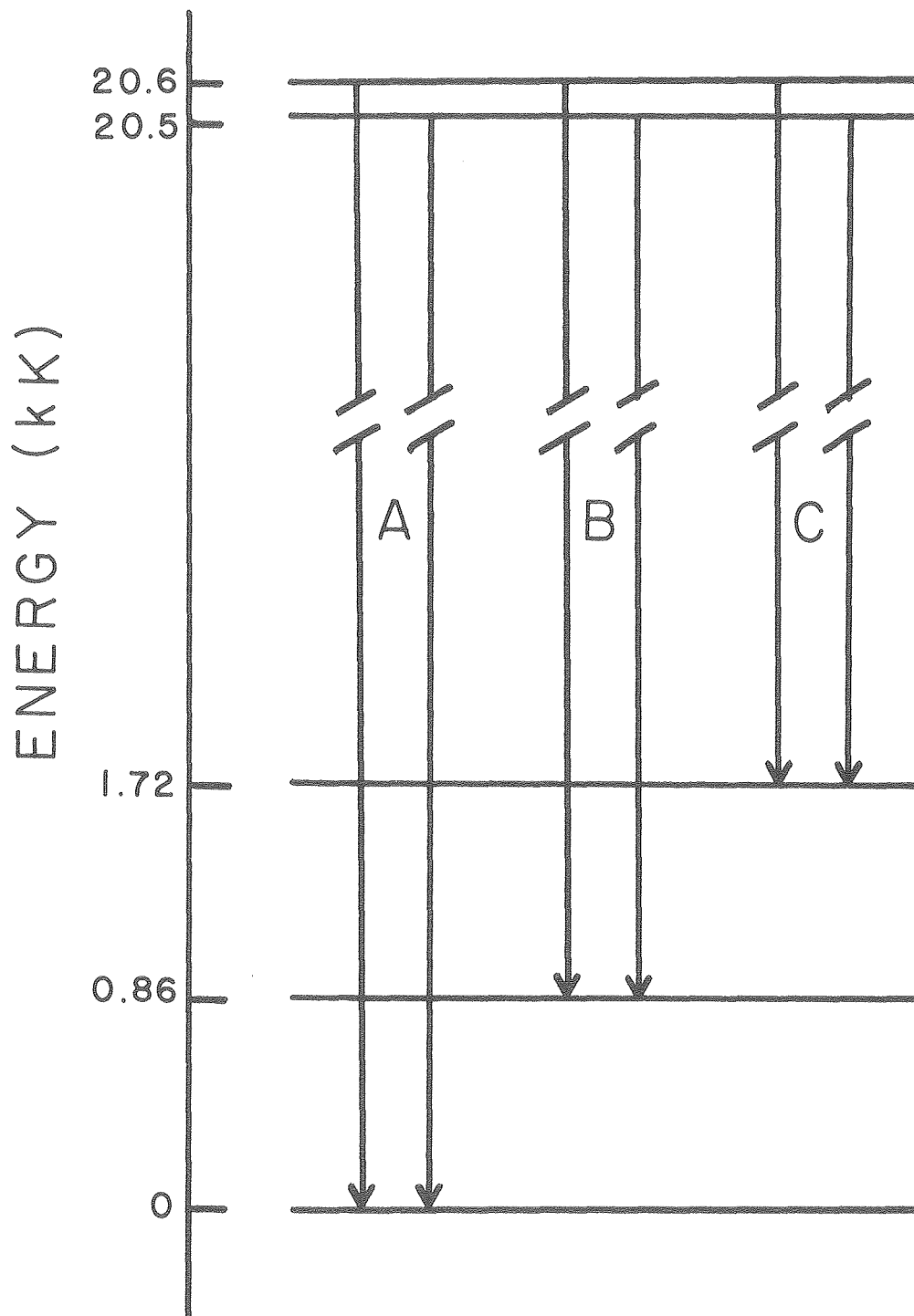


Figure 5. Luminescence at 77°K for the UNI (lower) and UNH (upper) complexes; this emission is from band system B. While the intensity scales are arbitrary, the UNI peak at 5068 Å has been reduced by a factor of 3.



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Figure 6. Luminescence at 77°K for the UNI (lower) and UNH (upper) complexes; this emission is from band system C. The intensity scales are arbitrary.



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Figure 7. Energy level diagram relating the luminescence peaks at 77°K to the energies of the various electronic states.

Table I. Wavelengths and energies of the luminescence bands of uranyl nitrate hexahydrate (UNH) at 77°K.

Band	Wavelength maximum (Å)	Energy (cm ⁻¹)
A	4855	20,597
	4875sh	20,515
B	5068	19,732
	5089	19,650
C	5301	18,864
	5324	18,783

Table II. Wavelength and energies of the luminescence bands of di-μ-aquo-bis(dioxobis(nitrato)uranium(VI)) (UNI) at 77°K.

Band System	Wavelength maximum (Å)	Energy (cm ⁻¹)	Assignment
A	4813	20,777	v ₁ = 0
	4829	20,708	v ₂ = 0
	4853	20,606	v ₁ = 1
	4873	20,520	v ₂ = 1
	4894	20,433	v ₁ = 2
	4912	20,358	v ₂ = 2
	4940	20,243	v ₁ = 3
	4955	20,182	v ₂ = 3
B	5020	19,920	v ₁ = 0
	5036	19,857	v ₂ = 0
	5063	19,751	v ₁ = 1
	5085	19,666	v ₂ = 1
	5110	19,570	v ₁ = 2
	5129	19,497	v ₂ = 2
	5158	19,387	v ₁ = 3
	5178	19,312	v ₂ = 3
C	5246	19,062	v ₁ = 0
	5263	19,001	v ₂ = 0
	5292	18,896	v ₁ = 1
	5315	18,813	v ₂ = 1
	5340	18,727	v ₁ = 2
	5364	18,643	v ₂ = 2

